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Mimicking Catalytic Properties of Precious Metals by Using Common Metal Nanostructured Particles

Professor Renzo Rosei

**Consorzio per la Fisica
Department of Physics
Strada Costiera 11
Trieste, Italy 34151**

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14. ABSTRACT This project explores the design, synthesis and testing of novel core-shell nanoparticles, specifically conceived to closely mimic the catalytic activity of platinum, with the aim of providing an engineered substitute to platinum for industrial catalytic applications. A preliminary assessment (based on Norskov d-band model of catalytic phenomena) was conducted for finding transition metal couples, which arranged in core-shell geometry, would present a surface chemical reactivity close to that of platinum. This assessment used existing literature calculations and databases to identify ruthenium shell on nickel core and palladium shell on cobalt core as promising possibilities to mimic platinum reactivity. The research focused on the ruthenium-nickel system, including theoretical calculations using density functional theory, synthesis of Ru@Ni core-shell nanoparticles, nanoscale structural characterization, and comparison of catalytic activity to platinum in a test reaction (ammonia borane dehydrogenation). In addition, Ni-Ru "alloy" nanoparticles were synthesized and their reactivity compared to that of the Ru@Ni core-shell nanoparticles and platinum. Both the Ru@Ni core-shell nanoparticles and the Ni-Ru "alloy" nanoparticles showed catalytic activity much higher than that of individual base metals, and in the latter case, the reactivity was quite close to that of platinum for the test case reaction. The results are encouraging to engineer substitutes to precious metals, however further tests are needed to check reactivity for other reactions of interest and ensure stability of the catalytic nanoparticles under harsher conditions (e.g., higher temperatures and/or more reactive gas environments).					
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MIMICKING CATALYTIC PROPERTIES OF PRECIOUS METALS BY USING COMMON METAL NANOSTRUCTURED PARTICLES

R. Rosei

*Physics Department, University of Trieste, Trieste, Italy
and
Consorzio per la Fisica, Trieste, Italy*

1. Project motivation and Synopsis of activity

- **PLATINUM** is a key material for a number of industrial and economic activities [like e.g. gasoline production through catalytic oil hydro-cracking, synthesis of explosives through ammonia oxidation reactions and many others]. Ever larger worldwide consumption, declining production, and geopolitical reasons have raised a widespread international concern about Platinum near-future availability [1]. For this reason Platinum has recently reached an overall **strategic importance** and it has been classified among the so-called *critical metals* [2].

The present EOARD project deals with the design, synthesis and testing of **novel core-shell catalyst nano-particles, specifically conceived to closely mimic the catalytic activity of Pt**, with the aim of substituting a large part of industrial Platinum's uses as a catalyst.

The rationale of the present project has already been presented at the research proposal stage. For completeness, however, an abridged version is reported in Annex 1.

A preliminary assessment (according to the guideline in Annex 1) was conducted for finding Transition Metals couples, which arranged in Core-Shell geometry, would present a surface chemical reactivity close to Platinum's. This preliminary job was conducted by consulting existing literature calculations [3] and databases [4]. This assessment activity showed that two different TM couples have promising possibilities to be engineered to present the desired properties:

- A) Ruthenium shell on a Nickel core (Ru@Ni);
- B) Palladium shell on a Cobalt core (Pd@Co).

In the present report we illustrate the work done on the Ru@Ni system.

The approach of the present project combines:

- 1) Advanced theoretical calculations;
- 2) Core-shell nano-particle synthesis;
- 3) Advanced nano-scale structural characterization techniques;
- 4) Assessment of the new catalyst's catalytic activity with respect to Platinum's in a test catalytic reaction (Ammonia Borane dehydrogenation).

2. Results

2.1 DFT Calculations

In a number of breakthrough papers [3] it has been shown that the energy of the Center of the d-band of a TM is a good indicator of the element's chemical reactivity. This quantity is amenable to be reliably obtained through Density Functional Theory calculations. In the following, the calculations performed on a number of model catalysts' surfaces are described. Although these calculations cannot replace *bona fide* catalytic experiments, still they are invaluable in restricting the pool of promising systems.

2.1.1 Technicalities

As already mentioned, a good descriptor of a TM surface catalytic activity is the position of the centre of the d band, defined as follows:

$$E_d = \frac{\int_{-\infty}^{E_0} dE (E - E_F) p_d(E)}{\int_{-\infty}^{E_F + E_0} dE p_d(E)} \quad (1)$$

Where E_F is the Fermi energy, $p_d(E)$ is the projection of the electronic density of states onto atomic orbitals of type d, and E_0 is a cut-off energy that we choose to be 5 eV above the Fermi energy. For a magnetic system like Ni one can define two d centres, one for the d band holding spin-up electrons and one for the spin-down electrons, and also an average centre by taking the sum of the two partial density of states.

Related to this quantity is the width of the band, defined as the second moment of the energy:

$$W = \frac{\int_{-\infty}^{E_0} dE (E - E_F - E_d)^2 p_d(E)}{\int_{-\infty}^{E_F + E_0} dE p_d(E)} \quad (2)$$

And finally, we are also interested in the occupation of the d band, defined as follows:

$$N_d = \int_{-\infty}^{E_F} dE p_d(E) \quad (3)$$

Similar quantities can be defined for the spin-polarised case, and in general we will be interested in the average quantities obtained by summing the two partial density of states.

The calculations have been performed using density functional theory (DFT) with the generalised gradient corrections (GGA) of Perdew, Burke & Ernzerhof known as PBE [5]. The ionic cores have been described using ultrasoft-pseudopotentials (USPP) [6] and single particle orbitals expanded in plane waves with a plane-wave cutoff of 30 Ry, and a cutoff for the charge density of 240 Ry. The code used for the calculations was PWscf [7]. Surfaces have been modelled using slab geometry, with five atomic layers and a vacuum region of 12 Å. Two atomic layers have been fixed to the bulk inter-atomic distance and only the topmost three atomic layers have been allowed to relax, when needed. Convergence with respect to the thickness of the vacuum region has been carefully tested.

Integration inside the Brillouin zone (BZ) has been performed by summation over 12x12x1 Monkhorst-Pack grids of special points. A smearing function of Methfessel-Paxton [8] (product of a Gaussian times a first order Hermite polynomial) and width = 0.13 eV has been used throughout.

2.1.2 Calculations

Besides calculating the center of mass of the d band, it was decided to calculate also the molecular-hydrogen energy desorption energy, which we expect to be a useful parameter for the catalytic tests (ammonia borane dissociation, *vide infra*) of our catalysts.

The calculations were performed for the Ni(111), Ru(0001), Ni₃Ru(111), Ru@Ni(111) and 2Ru@Ni(111) surfaces. The same calculations were also made for a Pt(111) surface, which gives us the necessary reactivity benchmark. The calculations refer in each case to the fcc(111) surface, except for Ru, where the hcp(0001) surface was considered. The Ru@Ni system refers to a geometry in which a Ru Monolayer is deposited on a Ni(111) surface and the 2Ru@Ni system refers to a geometry in which two Ru Monolayers have been deposited on Nickel.

Table 1 reports the calculated Center of mass of the d band (E_d) and the hydrogen desorption energy E_H^{des}) for all the model catalysts tested.

Table 1. Calculated d-band center of mass and hydrogen desorption energy for the catalytic model surfaces tested.

System	Ru@Ni	2Ru@Ni	Pt	Ru	Ni ₃ Ru	Ni
E_d (eV)	-2.40	-2.12	-2.08	-1.77	-1.68	-1.44
E_H^{des} (eV)	0.48	0.72	0.74	1.11	1.23	1.43

Fig. 1 reports in graphical form the calculated Hydrogen Desorption Energy E_H^{des} and the Center of mass Energy of the d band (E_d) for the various tested metal systems.

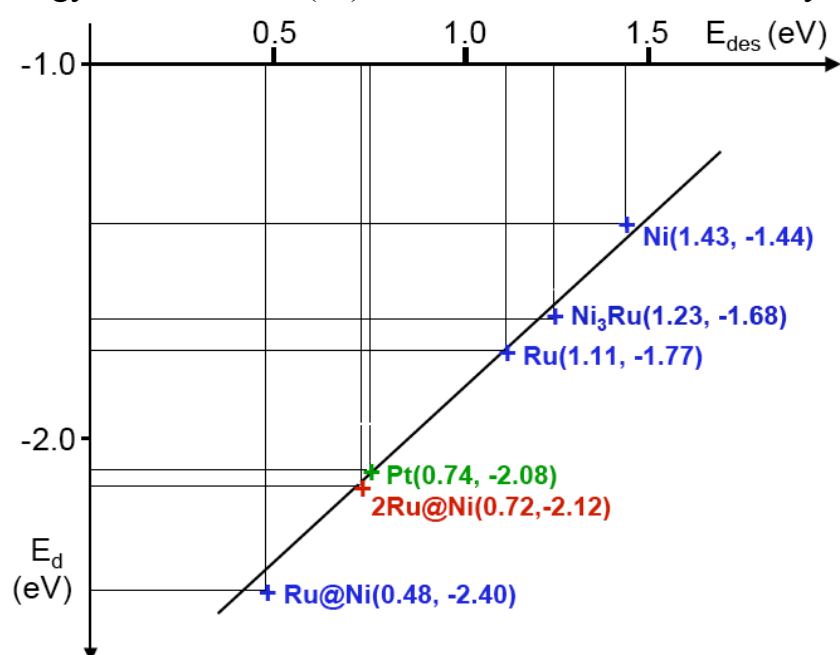


Figure 1. Plot of the hydrogen desorption energy versus the d-band center of mass for the TM and TM inter-metallic combinations tested.

As expected, calculated values are nicely aligned, confirming that hydrogen desorption energy can also be taken as a reliable chemical reactivity indicator. Most importantly, Fig. 1 shows that the 2Ru@Ni(111) sample has both indicators very close to Platinum's, and that it could be therefore a good candidate as Platinum replacement in catalytic reactions.

2.2 Synthesis method [first approach]

We proceeded in synthesizing core shell Ru@Ni nanoparticles, in a form suitable to be tested in a catalytic reactor setup. Besides the core shell samples, we have synthesized a number of other catalysts for comparison purposes. All synthesis procedures were carried out using standard airless methods, with Ar flow as inert gas.

(1) Synthesis of Ni nanoparticles.

In a typical synthesis, nickel (II) acetylacetonate (64 mg) were dissolved in diphenyl ether (5 ml) containing oleic acid (0.75 ml). The solution was heated to 120 °C and kept at this temperature for 20 min to remove humidity and oxygen. Next, the solution was cooled down to 90 °C, and 1 ml of Superhydride® was injected into the solution. After 1 min, the as-prepared mixture was transferred into a flask containing 15 ml of oleylamine, which was preheated to 300 °C. The mixture was kept at 250 °C for 15 min;

(2) Synthesis of Ni@Ru core-shell NPs.

The colloidal suspension of Ni seeds (1) was cooled down and an oleylamine solution (4 ml) containing Ru₃(CO)₁₂ (53.3 mg) was injected at 100 °C. The as-obtained mixture was heated to 180 °C under vigorous stirring, and then slowly brought to 200 °C. The reaction was quenched by removing the reaction flask off the mantle, after refluxing for 30 min. Ethanol (40 mL) was added and the product was separated by centrifugation at 9000 rpm for 10 min. The product was then dispersed in hexane.

(3) Synthesis of Ru NPs.

Ru₃(CO)₁₂ was ultrasonicated in oleylamine (15 ml) for 30 min to get a transparent crimson solution. The as-prepared solution was heated to 200 °C and kept at this temperature for 30 min. The solution was cooled down to room temperature. Ethanol (40 mL) was added and the product was separated by centrifugation at 9000 rpm for 10 min. The product was then dispersed in hexane.

2.3 Sample Characterization

In order to assess sample morphology we carried out several experiments using many different characterization techniques.

Powder X-ray diffraction (XRD) was performed on a Philips X'pert Diffractometer using a Cu K α radiation source ($\lambda = 0.154$ nm). X-ray photoelectron spectra (XPS) were taken using a VG Escalab 220i-XL equipped with an Al source. The etching was carried out by Ar sputtering under the conditions of a background vacuum of 2.0×10^{-8} mbar, a sputtering acceleration voltage of 3.0 kV and a sputtering current of 100 nA.

Transmission electron microscopy (TEM, JEOL 2100F) and energy-dispersive X-ray spectroscopy (EDS) were applied for a detailed analysis of microstructure and composition.

The TEM and EDS samples were prepared by depositing one or two droplets of the NPs colloidal suspension in hexane onto copper grids coated with thin carbon film.

A TEM image of Ru@Ni core-shell NPs is shown in Fig. 2.

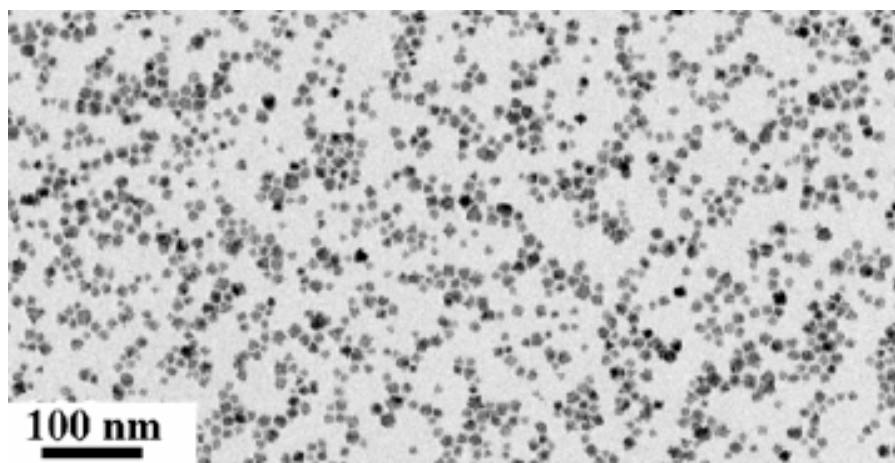


Figure 2. TEM image of the as-prepared Ru@Ni core-shell NPs

The average size of Ni and Ru@Ni NPs is 12.5 and 15.0 nm, respectively. The Selected Area Electron Diffraction (SAED) pattern for Ni@Ru NPs (Fig. 3) exhibits two sets of diffraction rings, one set corresponding to the fcc structure of Ni, the other corresponding to the hcp structure of Ru in the Ni@Ru core-shell NPs.

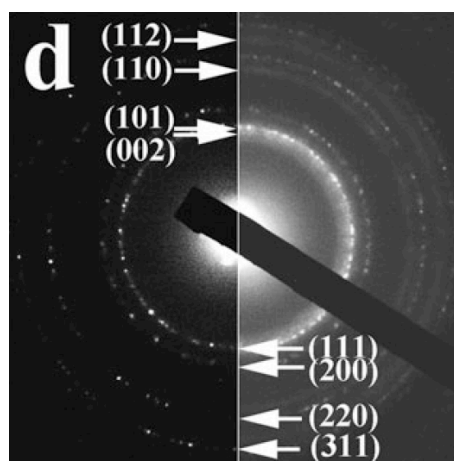


Figure 3. SAED patterns of Ni (left) and Ru@Ni (right) core-shell NPs, respectively. The indexes of crystal planes in the upper left refer to Ruthenium and those in the lower right to Nickel.

In order to further confirm the NPs core-shell morphology, the as-prepared sample was fully characterized by a combination of X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

2.4. Catalytic tests

Hydrolysis of Ammonia-Borane (AB) was chosen as a model reaction to evaluate the

catalytic properties of Ru@Ni core-shell NPs. This reaction is an interesting test-bench because Platinum is the best-known catalyst for this promising process. Indeed, the AB complex was recently identified as an attractive candidate for hydrogen storage, because of its high hydrogen content (19.6 wt%). Hydrogen hydrolysis yields 3 mol of hydrogen per mol of AB at room temperature, in the presence of a suitable catalyst [9].

In our tests, the amount of generated H₂ was measured by an inverted and graduated burette filled with water. All the tested NPs were first loaded onto electro-conductive carbon black (Ketjenblack EC-300J) with high specific surface area (~800 m²g⁻¹) and then dispersed in water without any special treatment, in order to remove surface capping ligands.

Fig. 4 shows the hydrogen evolution vs. time from an aqueous solution of AB in the presence of monometallic Ni and Ru, and of Ru@Ni NPs.

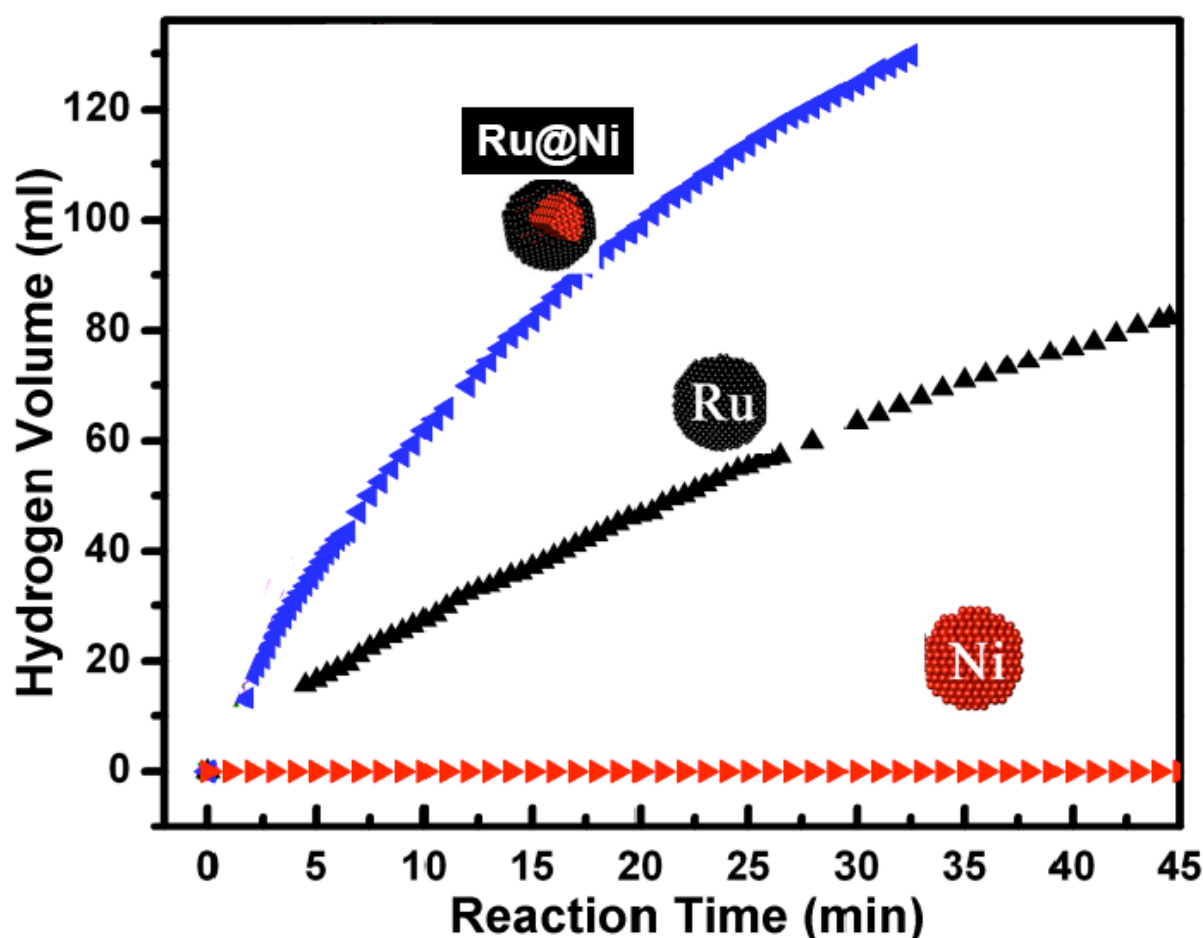


Figure 4. Volume of hydrogen evolution versus time, for the catalyzed Ammonia Borane hydrolysis reaction. The catalysts employed were Ni, Ru and Ru@Ni nanoparticles.

There is essentially no gas release for Ni NPs even after 1 h, indicating that the Ni NPs are practically inactive. Monometallic Ru NPs instead exhibit catalytic activity, completing the AB hydrolysis reaction within ~1 hour.

The Ru@Ni core-shell NPs catalyst shows decisively higher activity than either the two pure metals. This is an indirect proof that the synthesized NPs are *bona-fide* core-shell nanoparticles. Indeed, separated pure metals, Ru and Ni, have both shown a lower activity, and random RuNi alloy NPs catalysts would be expected to have an activity *intermediate* between Ruthenium's and Nickel's [10].

By repeating the kinetic measurements at several different temperatures (in the range $20\text{ }^{\circ}\text{C} > T > 60\text{ }^{\circ}\text{C}$), and constructing an Arrhenius plot in each case, we have been able to determine the apparent activation barriers of our different catalysts for the AB hydrolysis reaction. We obtain for Ru@Ni, Ru and Ni NPs, $44 \pm 3\text{ kJ mol}^{-1}$, 49 ± 4 and $70 \pm 5\text{ kJ mol}^{-1}$, respectively.

While this result is quite encouraging, still it is not what it had been expected from the calculations in the design phase. A high resolution TEM image of our Ru@Ni NPs shows the likely reason of this discrepancy (see Fig. 5)

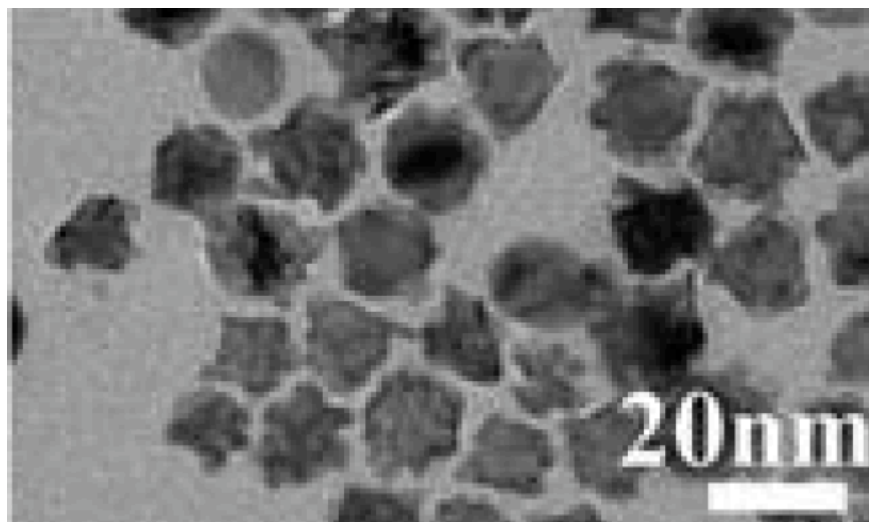


Fig. 5. High resolution TEM image of a Ru@Ni NPs collection

After the Ru-shell deposition, most of the Ni@Ru NPs do not inherit the initial spherical shape of the Ni NPs, but exhibit rough surfaces with irregular features. This rugged morphology (most likely originating from the rather large Ni-Ru atomic radius mismatch) certainly affects NPs' chemical reactivity, beyond the initial design parameters.

For this reason, we have attempted a different synthesis route.

2.5 Alternative synthesis approach

Nickel and Ruthenium have a large standard reduction potentials difference, and this suggests that a fast reduction process may allow trapping Ni and Ru atoms into non-equilibrium configurations, avoiding at the same time separate nucleation. In this second synthesis method, a strong reducing agent, a preheated precursor solution and a high-boiling solvent were employed. Ni-Ru NPs were prepared using a hot-injection method with co-reduction of $\text{Ni}(\text{acac})_2$ and $\text{Ru}(\text{acac})_3$ (acac=acetylacetonate) in oleylamine, using Super-Hydride (LiBEt_3H), as reducing agent. Oleylamine and oleic acid were employed as capping agents to control particle size. With this procedure we obtained Ni-Ru bimetallic NPs with several different Ni/Ru atomic ratios.

Figure 6 reports a representative TEM image of a NPs sample (synthesized through this second route), with a Ni/Ru ratio of 0.74/0.26, showing rounded particles of $\sim 9\text{ nm}$ average diameter. Similar morphologies and sizes were observed for NPs samples with Ni/Ru ratios of 0.63/0.37 and 0.56/0.44.

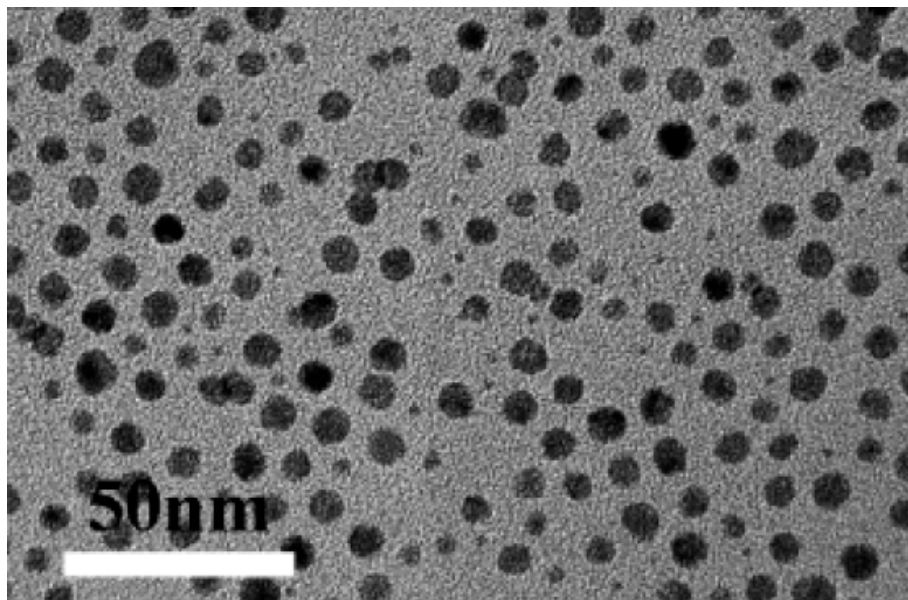


Figure 6. TEM image of a Ni/Ru bimetallic NPs collection, with Ni/Ru atomic ratio of 0.74/0.26. In this case NPs mostly keep a round regular structure.

XRD patterns of as-prepared NPs with different Ni/Ru concentration ratio are reported in Figure 7, where also the expected major peak positions of Ni (fcc structure), and Ru (hcp structure), are marked. All the tested samples exhibit fcc structure reflections, indicating the formation of fcc metallic alloys. The diffraction peaks shift to lower angles as the atomic percentage of Ru increases, demonstrating a lattice expansion originating from the progressive substitution of the larger Ru atoms in place of the smaller Ni atoms.

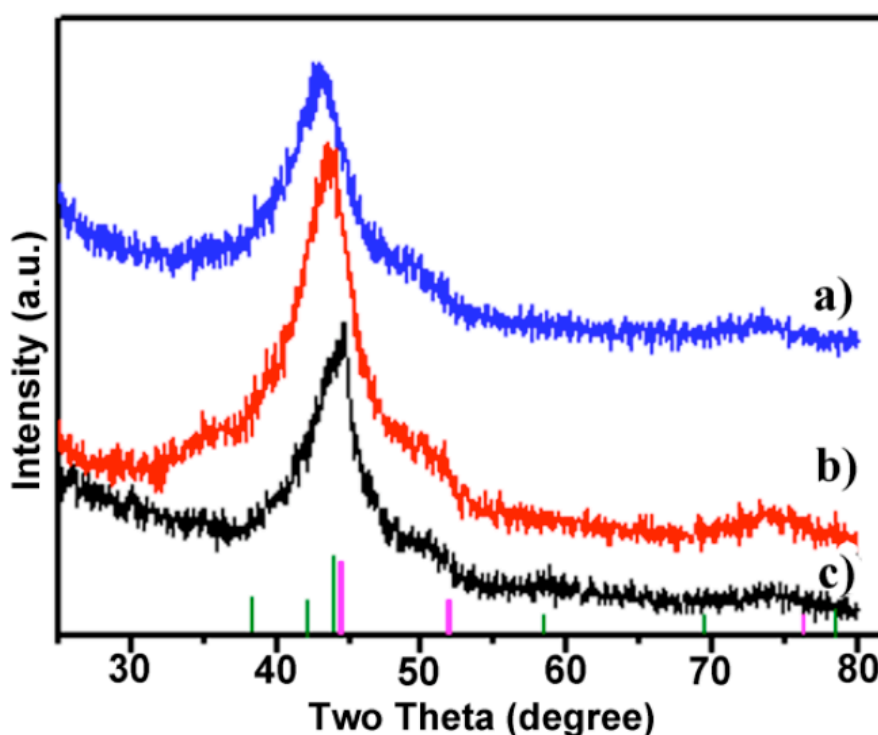


Figure 7. XRD patterns of Ni/Ru NPs with different concentration ratios: (a) Ni/Ru = 0.56/0.44; (b) Ni/Ru = 0.63/0.37; (c) Ni/Ru = 0.74/0.26. Green vertical lines represent the hcp Ru phase and pink vertical lines the fcc Ni phase

The activity of Ni-Ru alloy NPs with different compositions was evaluated for the AB dehydrogenation reaction, and the results were compared to the activity of similar size monometallic Ni and Ru, and of Ni@Ru core-shell NPs (previously displayed). Figure 8 reports a comparison of the hydrogen evolution curves during the AB hydrolysis reaction. The new bimetallic Ni-Ru NPs appear to be a much better catalyst than pure Ru or Ni, or even than our previously synthesized Ru@Ni NPs. Definitely, the catalytic activity improvement of our Ni-Ru bimetallic NPs in comparison with monometallic Ru, indicates a chemical effect well beyond the simple physical addition of Ni.

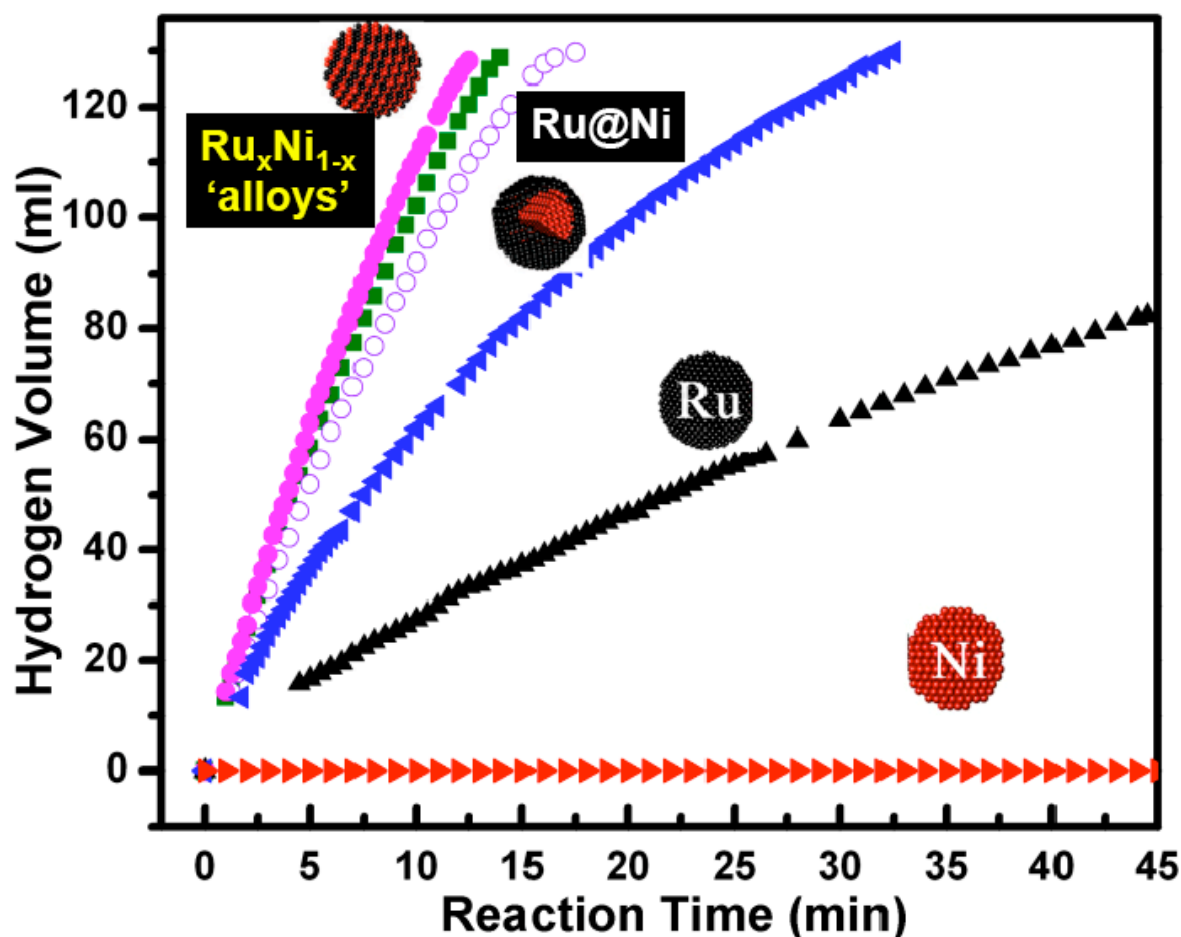


Figure 8. Comparison of catalytic activities of monometallic Ni, monometallic Ru, Ni@Ru core-shell and Ni-Ru alloy NPs (pink: Ni/Ru = 0.74/0.26; green: Ni/Ru = 0.63/0.37; purple: Ni/Ru = 0.56/0.44), for AB hydrolysis at 30±1°C.

These results are very interesting but also not straightforward to explain at first sight. In essence we have found that we can obtain a much better catalyst for the AB hydrolysis reaction by forming an alloy between Ni (which is not active for the reaction), and Ru, which is only mildly active. Besides, a comparison with literature results [11] shows that this catalyst's activity is fairly close to the activity of Platinum. Both these findings are difficult to reconcile with a NPs' surface structure where Ni and Ru are randomly interspersed (because in this case the reactivity should have an intermediate value between Ni and Ru, which is obviously not the case). Tentatively, our results can be explained by a NPs surface structure consisting of one monolayer thick islands of Ru atoms (surrounded by Ni atoms). This is plausible because Ru-Ru bonds are stronger than Ru-Ni bonds and NPs' surface atoms are quite mobile even at low temperature. The 'bulk' of the

nanoparticles instead, consists of homogeneous RuNi alloys (as shown by our characterization techniques).

Nanostructures of this type have already been reported in the literature, especially in connection with fuel cells electrocatalysts. See for instance Adzic et al. [12].

According to the d-band model [3], the activity of Ruthenium islands' atoms (which sit mostly on second layer Ni atoms), would be lowered by a synergic combination of strain (because Ru atomic radius is larger than the radius of Ni) and ligand effects. The concerted action of these two effects would lower the projected center of the d-band (with respect to the Fermi Surface), thus lowering the local chemical reactivity (towards values close to Platinum's) [3].

Figure 9 shows an heuristic model of our new Ni/Ru bimetallic NPs, which we can tentatively identify as "Ru-skin@RuNi-alloy" nanoparticles.

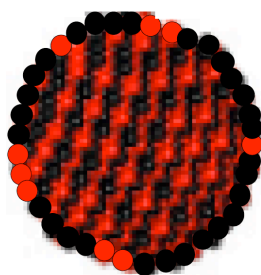


Figure 9. Envisioned model of our Ru-Ni "alloy" NPs. While NPs' "bulk" consists of a random homogeneous Ru-Ni alloy, the outer surface layer is largely formed by one-monolayer thick islands of Ru atoms (which act as active sites for the AB hydrolysis reaction).

At the moment we still don't have a direct proof of this envisioned morphology (which most likely will need Aberration Corrected Ultra HRTEM instrumentation to be resolved). Further work is therefore needed to prove (or disprove) this model and, especially, to check whether it is possible to further tailoring the catalytic activity of the system and steer it towards values closer to Platinum's activity.

3. Conclusions

A series of activities have been carried out within the scope of EOARD Contract #103060, with the aim of individuating a Transition Metal bimetallic system presenting catalytic activity similar to Platinum. Preliminary consultation of existing databases on TM chemical reactivity, atomic radii, and segregation energies, has allowed pinpointing the Ru@Ni core-shell system as a promising candidates. DFT calculations of chemical reactivity descriptors of several TM systems, confirmed that Ru@Ni was indeed a suitable candidate for tailoring catalytic activity so that it would result close to Platinum's.

Accordingly, Ru@Ni core-shell nanoparticles were synthesized and thoroughly characterized using several advanced experimental techniques.

A different series of Ru-Ni bimetallic NPs systems was also synthesized, which structure appears as consisting of homogeneous random Ni-Ru alloys.

Finally, the Ru@Ni and the Ni-Ru 'alloys' NPs catalysts were tested against pure Ni and Ru catalysts, in the Ammonia Borane hydrolysis reaction. Both catalysts, and in particular the Ni-Ru 'alloys', showed a catalytic activity much higher than the activity of the single

constituent metals. In the latter case actually, the catalytic activity approaches the activity of Pt nanoparticles.

The high activity of the Ni-Ru ‘alloys’ NPs can be rationalized by a structural model in which “bulk” Ni-Ru alloy NPs are covered by a ‘skin’ of Ru atoms just one monolayer thick. This model, however, needs to be confirmed by more sensitive structural techniques (like, for instance, Aberration Corrected HRTEM).

Our results are very encouraging. However, further tests are needed to check our NPs activity in other reactions. In particular, the stability of the new catalyst should be tested in harsher conditions (like e.g. more reactive reactant gases and higher temperatures).

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Annex 1

Recent advances in understanding catalytic phenomena by the Norskov School [A1], have allowed implementing calculations (the so called d-band model), to predict **chemical reactivity** and **catalytic activity** of different transition metals stoichiometry in different geometrical configurations. In short, a Transition Metal (TM) ‘A’ chemical reactivity depends not only on its own elemental identity, but also on the identity of neighboring TM atoms (ligand effect) and on the stress/strain state of its local geometrical arrangement.

These same concepts lead to envisioning a completely new way for manipulating nanoparticles’ chemical reactivity. By producing core-shell geometries with TM metal **A** atoms in the core, and TM metal atoms **B** in the shell, the catalytic properties will depend not only on B elemental identity, but also on the ligand and stress effects originating from the A metal in the core [A2].

An appropriate choice of A and B metals may allow therefore implementing a first principle design of the particle reactivity. In particular, it should be possible to arrange the

composition in such a way that the particle reactivity is identical to Platinum particles' (of similar size).

Annex 1 References.

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